Calculations of the shear modulus of a two-dimensional quantum solid

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The elastic moduli for a two-dimensional triangular lattice at zero temperature are calculated with Hartree, Jastrow, and semiclassical approximations to the variational quantum theory. Results are presented for Lennard-Jones (12,6) potential models of helium, neon, and argon and are compared with available experimental data. The semiclassical approximation is used to discuss departures from the conditions for a Cauchy solid.

I. INTRODUCTION

The shear elastic modulus of a monolayer solid enters in the continuum approximations to the specific heat (Debye theory) and to the theory of orientational epitaxy (Novaco-McTague rotation).[1] In combination with the bulk modulus and the spreading pressure, it determines the ratio of the speeds of longitudinal and transverse sound.[2] It is a part of the analysis of whether the monolayer solid satisfies the conditions of a Cauchy solid.[3,4] The continuum description of a (two-dimensional) triangular lattice leads to an isotropic elasticity theory characterized by two Lamé constants, one being the shear modulus.

We report here calculations of the elastic moduli of two-dimensional quantum solids from derivatives of the ground-state energy. The calculations are aimed both at the development of the variational quantum theory, and at quantitative discussion of experimental data for monolayer solids which display large quantum effects. A determination of the shear modulus from ground-state calculations includes consideration of nontriangular lattices, in contrast to the sequence of triangular lattices used in calculating the monolayer bulk modulus.[5]

The work is based on Hartree and Jastrow variational approximations to the quantum-mechanical ground-state energy of triangular and nearly triangular lattices. The Jastrow trial function consists of a product of two-body correlation factors and one-body factors which are Gaussians centered on the lattice sites. Usually,[5–7] the Gaussians are taken to be circular symmetric. Noncircular-symmetric terms for the nontriangular lattices contribute in the energy derivatives for the shear modulus; they are here treated with a perturbation approximation to the Hartree and Jastrow variational calculations. There are large effects of correlated motions in the shear modulus of two-dimensional solid helium, as the differences between the results of the Hartree and Jastrow approximations show. The Hartree values have significant contributions (ca. 30%) from the corrections to circular symmetry for nearly triangular lattices; the contributions in the Jastrow values are smaller (ca. 5%).

An alternative approach, used for calculation of elastic constants of three-dimensional quantum solids, is the method of long waves with frequencies obtained from the self-consistent-phonon (SCP) approximation.[8] Since assumptions on the form of the many-body wave function also enter there, information on the relative importance of terms in the ground-state calculation may have application to the SCP theory. It will be useful in the future to compare elastic constants obtained from the Hartree and the SCP approximations[9,10] for systems such as argon and neon where the short-range quantum correlations do not have large effects in the elastic moduli.

A related set of questions has to do with the inclusion in the variational trial function of factors which reflect the lattice symmetry, such as Rosenwald's use[11] of Kubic harmonics in the Hartree theory of three-dimensional body-centered-cubic ^{3}He. We estimate the effects in the Hartree ground-state energy of sixfold symmetric terms in the wave function for the triangular lattice and fourfold symmetric terms for the square lattice with a perturbation approximation similar to the shear modulus theory: Our limited search has no regime, within the Hartree approximation, where the square lattice is more stable than the triangular lattice.

For a classical triangular lattice at zero spreading pressure, with atoms interacting by pair potentials, the ratio of the squares of the speeds of longitudinal and transverse sound is 3, and in many model calculations the value of the ratio remains close to this. However, in the analysis by Greif and Goodstein[2] of data for monolayer solids of ^{3}He and of ^{4}He on graphite, the values range from 11 to 5, decreasing with increasing solid density. For the Jastrow calculation the values range from 2.4 to 4 and increase with increasing solid density.

The organization of this paper is as follows: Section II contains the formalism for determining elastic constants from ground-state energy calculations, with Hartree, Jastrow, and semiclassical approximations, and a discussion of a generalization of the Cauchy relation for the Lamé constants. Section III contains the results of the calculations and comparisons to experimental data for the elastic moduli and Debye temperatures. Section IV contains concluding remarks. The comparison of the triangular and square lattices is deferred to Appendix A; the first quantum corrections in the Hartree approximation are presented in Appendix B.

II. ELASTIC MODULI FOR TWO-DIMENSIONAL TRIANGULAR SOLIDS

A. Elasticity including a static stress

The deformation tensor μ_{ij} for a displacement of x to x',

$$x_i' = x_i + \sum_j u_{ij} x_j \ , \tag{2.1}$$

is used to define the Lagrangian stress tensor

$$\eta_{ij} = \tfrac{1}{2}\left[u_{ij} + u_{ji} + \sum_k u_{ki} u_{kj}\right] , \tag{2.2}$$

and the energy shift, for a solid of initial area A, is[12]

$$\Delta E = \int_A d^2 r \left[\sum_{i,j} S_{ij}\eta_{ij} + \tfrac{1}{2}\sum_{ij,kl} C_{ij,kl}\eta_{ij}\eta_{kl}\right] . \tag{2.3}$$

If the solid is initially in a state of isotropic stress with spreading pressure ϕ, the S coefficients are

$$S_{ij} = -\phi\delta_{ij} \ . \tag{2.4}$$

With a Voigt notation for the pairs of indices on the coefficient of the quadratic term,

$$1 = xx, \quad 2 = yy, \quad 3 = xy = yx \ , \tag{2.5}$$

the energy shift for a two-dimensional solid initially in a triangular lattice is

$$\Delta E = \int_A d^2 r \left[-\phi\left[\sum_i \eta_{ii}\right] + \tfrac{1}{2} C_{12}\left[\sum_i \eta_{ii}\right]^2 + C_{33}\sum_{ij}(\eta_{ij})^2\right] . \tag{2.6}$$

The coefficients for the triangular lattice satisfy the relations

$$C_{11} = C_{22}, \quad C_{11} = C_{12} + 2C_{33} \ , \tag{2.7}$$

and the speeds of longitudinal and transverse sound are[2]

$$\begin{aligned} c_l^2 &= \Gamma_{11}/\rho \ , \\ c_t^2 &= \Gamma_{33}/\rho \ , \end{aligned} \tag{2.8}$$

where ρ is the mass density and the coefficients Γ are

$$\begin{aligned} &\Gamma_{11} = C_{11} - \phi, \quad \Gamma_{33} = C_{33} - \phi \ , \\ &\Gamma_{12} = C_{12} + \phi \ . \end{aligned} \tag{2.9}$$

The square of the ratio of the sound speeds is related to the Poisson ratio[3] σ_2 for the triangular lattice by

$$R_s = \Gamma_{11}/\Gamma_{33} = 2/(1-\sigma_2) \ . \tag{2.10}$$

The relation to the Lamé constants λ and μ of isotropic elasticity theory is

$$\lambda = C_{12}, \quad \mu = C_{33} \ . \tag{2.11}$$

A Cauchy solid[3,13] is defined to have

$$\lambda = \mu \ . \tag{2.12}$$

Two special cases of the deformation tensor are used in the variational calculations. For an isotropic dilation

$$u_{ij} = \delta\delta_{ij} \ , \tag{2.13}$$

the energy shift is given by the bulk modulus B so that

$$B = (C_{11} + C_{22} + 2C_{12})/4 = C_{12} + C_{33} \ . \tag{2.14}$$

For a rectangular deformation at constant area

$$u_{ij} = \left[\frac{-\delta}{1+\delta}\right]\delta_{xx} + \delta\delta_{yy} \ , \tag{2.15}$$

the energy shift from the triangular lattice is

$$\Delta E = 2A(C_{33} - \phi)\delta^2 + O(\delta^3) \ , \tag{2.16}$$

in terms of the shear elastic modulus.

In all the calculations of this paper, the pair potential is the Lennard-Jones (12,6) model

$$\begin{aligned} \phi(r) &= 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \\ &= \varepsilon[(r_0/r)^{12} - 2(r_0/r)^6] \ , \end{aligned} \tag{2.17}$$

with the de Boer parameter defined by

$$\Lambda^* = h/(\sigma\sqrt{m\varepsilon}) \ . \tag{2.18}$$

The length and energy parameters σ and ε are used to define scaled energies $E^* = E/\varepsilon$, pressures $\phi^* = \phi\sigma^2/\varepsilon$, and elastic constants $C_{ij}^* = C_{ij}\sigma^2/\varepsilon$.

B. Hartree variational theory

The Hartree approximation is a generalization of the Einstein oscillator model of a solid, and is a step in the development leading to the treatment of the correlations required for solids of helium and hydrogen. It overestimates the zero-point energy in the harmonic approximation by only 5%;[14] as found here, the overestimate in the shear modulus is larger.

The Hartree trial function for N atoms with positions r_j centered on a lattice of sites R_j is

$$\Psi = \prod_{j=1}^{N} \psi(\mathbf{r}_j - \mathbf{R}_j) \ , \tag{2.19}$$

with normalized one-body functions ψ. The trial energy per atom is

$$E/N = (\hbar^2/2m)\int d\mathbf{u}\,|\,\nabla\psi\,|^2 + \tfrac{1}{2}\int d\mathbf{u}_1 d\mathbf{u}_2 V(\mathbf{u}_1 - \mathbf{u}_2)\,|\,\psi(\mathbf{u}_1)\psi(\mathbf{u}_2)\,|^2 \ , \tag{2.20}$$

for particles of mass m and displacement vector $\mathbf{u}_j = \mathbf{r}_j - \mathbf{R}_j$. The potential energy for a deformation $\vec{\mathbf{u}}\cdot\mathbf{R}_j$ of the lattice is given in terms of a two-body interaction by

$$V(\mathbf{u}_1 - \mathbf{u}_2) = \sum_j \phi(\mathbf{v}_j + \vec{\mathbf{u}}\cdot\mathbf{R}_j) \ , \tag{2.21}$$

with $\mathbf{v}_j = \mathbf{R}_j + \mathbf{u}_1 - \mathbf{u}_2$.

Using the isotropic dilation, Eq. (2.13), in Eq. (2.21) leads to an expression for the Hartree pressure which is similar to a virial theorem

$$\phi=-(N/4A)\sum_j \int d\mathbf{u}_1 d\mathbf{u}_2 \mathbf{R}_j\cdot\nabla\phi(v_j)\,|\,\psi(\mathbf{u}_1)\psi(\mathbf{u}_2)\,|^2 . \tag{2.22}$$

A comparison of pressures from Eq. (2.22) with finite-difference calculations of the energy derivative $-dE/dA$ provides a test of the internal consistency of numerical solutions of the Hartree equation.

The treatment of the deformation, Eq. (2.15), leading to the shear modulus via Eq. (2.16), is in two stages. First, under the added assumption that the Hartree wave function is circularly symmetric in both the triangular lattice and the deformed lattice,

$$\psi(\mathbf{u})=\psi(\,|\,\mathbf{u}\,|\,) , \tag{2.23}$$

the calculation of the energy shift becomes equivalent to a first-order perturbation theory calculation. Expansion of Eq. (2.21) to second order in δ leads to the following sums (prime denotes derivatives):

$$\begin{aligned} V_0&=\sum_j \phi(v_j) ,\\ V_2&=\sum_j \left[\tfrac{1}{4}R_j^2\left[\phi''(R_j)-\frac{1}{v_j}\phi'(v_j)\right]\right.\\ &\quad\left.-\frac{1}{2v_j}\phi'(v_j)\mathbf{R}_j\cdot(\mathbf{u}_1-\mathbf{u}_2)\right] \end{aligned} \tag{2.24}$$

and the energy shift is

$$\Delta E_1=-2(A\phi\delta^2)+(N\delta^2/2)\int d\mathbf{u}_1 d\mathbf{u}_2 V_2\,|\,\psi_0(u_1)\psi_0(u_2)\,|^2 . \tag{2.25}$$

The one-body wave function ψ_0 is the ground-state solution (energy ε_0) of the Hartree equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_0+\int d\mathbf{u}_2 V_0(\mathbf{u}_{12})\,|\,\psi_0(u_2)\,|^2\psi_0(u_1)=\varepsilon_0\psi_0(u_1) . \tag{2.26}$$

Second, the Hartree wave function is assumed to be circular symmetric in the triangular lattice, ψ_0, and to have an additional term proportional to $\cos(2\theta)$ in the deformed lattice,

$$\psi(\mathbf{u})=[\psi_0(u)+\gamma\tilde{\psi}(\mathbf{u})]/(1+\gamma^2)^{1/2} , \tag{2.27}$$

with

$$\tilde{\psi}(\mathbf{u})=\cos2\theta\psi_2(u) ,$$

where θ is measured from an "x axis" which is one of the primitive vectors of the triangular lattice. The factor $(1+\gamma^2)^{1/2}$ is inserted to maintain the normalization. The energy shift with this wave function is

$$\begin{aligned} \Delta E&=\Delta E_1+\Delta E_2 ,\\ \Delta E_2&=\gamma^2\left[\frac{\hbar^2}{2m}\int d\mathbf{u}\,|\,\nabla\tilde{\psi}\,|^2\right.\\ &\quad\left.+\int d\mathbf{u}_1 d\mathbf{u}_2 V_0\,|\,\psi_0(u_2)\tilde{\psi}(\mathbf{u}_1)\,|^2-\varepsilon_0\right]\\ &\quad+2\gamma^2A_2-2A_1\gamma\delta , \end{aligned} \tag{2.28}$$

with integrals A_1 and A_2 defined by

$$\begin{aligned} A_1&=\int d\mathbf{u}_1 d\mathbf{u}_2\,|\,\psi_0(u_1)\,|^2\psi_0(u_2)\tilde{\psi}(u_2)\\ &\quad\times\sum_j\frac{\phi'(v_j)}{v_j}(v_{jx}R_{jx}-v_{jy}R_{jy}) ,\\ A_2&=\int d\mathbf{u}_1 d\mathbf{u}_2 V_0\psi_0(u_1)\psi_0(u_2)\tilde{\psi}(\mathbf{u}_1)\tilde{\psi}(\mathbf{u}_2) . \end{aligned} \tag{2.29}$$

The wave function ψ_0 in Eqs. (2.25) and (2.28) is the lowest energy solution of the Hartree equation, Eq. (2.26). However, rather than also minimizing ΔE_2 by a functional optimization of $\tilde{\psi}$, we approximate $\tilde{\psi}$ with the lowest energy solution of

$$\left[-\frac{\hbar^2}{2m}\nabla^2+\int d\mathbf{u}_2 V_0\,|\,\psi_0(u_2)\,|^2\right]\cos2\theta_1\psi_2(u_1)=\varepsilon_2\cos2\theta_1\psi_2(u_1) , \tag{2.30}$$

and the coefficient γ is

$$\gamma=A_1\delta/(\varepsilon_2-\varepsilon_0+2A_2) . \tag{2.31}$$

This approximation is accurate in the near-classical regime ($\Lambda^*<0.2$) and gives the magnitude of the relative contribution of the $\tilde{\psi}$ term to the shear modulus for large Λ^*, where the correlations omitted from the Hartree trial function become important and have to be included by generalizations such as the Jastrow trial function.

C. Jastrow variational theory

We generalize slightly the conventional form[5–7] of the Jastrow trial function for a quantum Lennard-Jones solid

$$\Psi_j=\exp\left[-\tfrac{1}{2}\sum_{i<j}(b/r_{ij})^5-\frac{A}{2}\sum_j\mathbf{v}_j^2+\frac{A\Delta}{2}\sum_j(v_{jx}^2-v_{jy}^2)\right] , \tag{2.32}$$

where r_{ij} are interparticle distances, $v_j=r_j-R_j$ are the displacements from the average space lattice, and the x,y coordinate axes are those used in Eq. (2.15). This generalization of the ($\Delta=0$) form used previously for triangular lattices is analogous to that for the Hartree trial function, Eq. (2.27).

There are two series of calculations with Eq. (2.32). First, with $\Delta=0$, we find the minimum trial energy as a function of density for the triangular lattice, and for a triangular lattice deformed according to Eq. (2.15) with $\delta=0.05$. The energy differences at constant density correspond to ΔE_1, Eq. (2.25), of the Hartree theory. The energy expectation values are formed by Monte Carlo calculations for a grid of A,b values and McMillan scaling.[7] This finite difference approximation for the shear modulus is implemented with conventional methods.[5–7]

Second, we make an expansion to second order in Δ to generate the correction corresponding to ΔE_2 of the Hartree theory, Eq. (2.28). Because the optimal Δ, the scale of the non-circular-symmetric term, is proportional to δ, carrying the series to second order is sufficient for evaluating this contribution to the energy shift of Eq.

(2.16). The trial energy is, with expectation values $\langle \cdots \rangle$ taken with respect to the $\Delta=0$ case of Ψ_J,

$$E_J=N(\hbar^2 A/2m)+\tfrac{25}{8}b^5\frac{\hbar^2}{m}K_7+2\varepsilon(\sigma^{12}K_{12}-\sigma^6K_6)\ , \tag{2.33}$$

where

$$K_n=K_n(0)-\tfrac{5}{2}(A\Delta\delta)[K_n(2)-K_n(0)N_1] +(nA\Delta\delta)K_n(1)+\tfrac{1}{2}(A\Delta)^2[K_n(3)-K_n(0)N_2]\ . \tag{2.34}$$

The terms $K_n(p)$ and N_p are defined in terms of

$$S_n=\sum_{i\neq j}1/r_{ij}^n\ ,$$
$$s=\sum_j(v_{jx}^2-v_{jy}^2)\ , \tag{2.35}$$
$$\rho_{ij}=r_{ijx}R_{ijx}-r_{ijy}R_{ijy}\ ,$$

by

$$K_n(0)=\langle S_n\rangle,\quad K_n(3)=\langle S_n s^2\rangle\ ,$$
$$K_n(1)=\left\langle s\sum_{i\neq j}\rho_{ij}/r_{ij}^{(n+2)}\right\rangle\ ,$$
$$K_n(2)=\left\langle S_n s\sum_{i\neq j}\rho_{ij}b^5/r_{ij}^7\right\rangle\ , \tag{2.36}$$
$$N_1=\left\langle s\sum_{i\neq j}b^5/r_{ij}^7\right\rangle,\quad N_2=\langle s^2\rangle\ .$$

The energy E_J is a quadratic form in Δ which is minimized with a value of Δ which is proportional to the deformation parameter δ. The Δ terms are then explicitly quadratic in δ, so that their contribution to the shear modulus is calculated with the expectation values of Eq. (2.36) for the nondistorted (triangular) lattice.

In outline, the numerical procedures are as follows: The Monte Carlo calculations of the unperturbed expectation values are performed on a periodically repeated cell of 100 particles and are averaged over 450 000 configurations. The trial energies are then formed by using the method suggested by Nosanow *et al.*,[7] which is to perform a third-order least-squares fit of the expectation values as a function of the two variables A and b. A two-dimensional Newton-Raphson method is used to locate the A and b values at which the energy is minimized.

The Monte Carlo calculations for the perturbation terms are performed for a periodically repeated cell of 36 particles and are averaged over 925 000 configurations. The longer runs are necessary because the differences entering in Eq. (2.34) have subtractions of order-N^2 terms to leave order-N energies.

D. Semiclassical approximations to the elastic moduli

Results of numerical evaluations of the Hartree and Jastrow approximations to the energies ΔE_1 and ΔE_2 for helium, neon, and argon parameters are presented in Sec. III. Hartree calculations for small de Boer parameters show that an expansion to first power in the de Boer parameter is accurate for Λ^* in the range 0.1–0.25, which includes argon and methane. Forms for the Hartree shear modulus in the near-classical limit are given in Appendix B for a general pair potential, and also for the Lennard-Jones (12,6) model, Eq. (2.17). In this subsection, we compare several approximations to the elastic moduli in the near-classical limit, where substantial algebraic reduction of the calculations occurs.

The first quantum corrections, linear in the de Boer parameter, for the energy, pressure, and elastic moduli, are calculated precisely without a variational approximation by starting from the normal mode frequencies of small amplitude vibrations of the (distorted) lattice. Thus, strain derivatives of the zero-point energy, the zero-temperature limit of the quasiharmonic free energy,[14,15] lead to a nominally exact determination of the first quantum corrections which includes correlated motions. The results of the quasiharmonic theory[16] (QHT) give a first measure of the approximations in the Hartree and Jastrow variational theories. A comparison of the quasiharmonic, Hartree, and Jastrow values for the first quantum corrections is shown in Table I; the two near-neighbor spacings, $L/r_0=1.01$ and 0.985, span the range of zero-temperature monolayer lattice constants for a Lennard-Jones model of argon adsorbed on the basal plane surface of graphite.[17]

The entries in Table I are for the coefficients $E^{(1)*}$, $\phi^{(1)*}$, $B^{(1)*}$, and $C_{33}^{(1)*}$ in the expansion of the scaled ground-state energy, spreading pressure, bulk modulus, and shear modulus

$$E^*=E^{(0)*}+\Lambda^*E^{(1)*}+\cdots\ ,$$
$$\phi^*=\phi^{(0)*}+\Lambda^*\phi^{(1)*}+\cdots\ , \tag{2.37}$$
$$B^*=B^{(0)*}+\Lambda^*B^{(1)*}+\cdots\ ,$$
$$C_{33}^*=C_{33}^{(0)*}+\Lambda^*C_{33}^{(1)*}+\cdots\ .$$

The Hartree approximation provides a simple method of treating strongly anharmonic solids, and leads to relatively compact expressions for the quantum corrections, Appendix B, but it omits correlation effects. The accuracy of the Hartree linear quantum correction terms, given in Appendix B, was tested with Hartree calculations using the full formalism of Sec. II B for $l=L/r_0=1.01$ and values of Λ^* in the range 0.08–0.25. The values for C_{33} showed a linear variation with Λ^* and the slope was in good agreement with the value obtained from Eqs. (B14) and (B15). For $\Lambda^*=0.246$, corresponding to methane, C_{33} calculated from the Hartree equations is 24.9, while the classical mechanics value is 17.9; the quantum correction calculated with Eqs. (B14) and (B15) reproduces the change from the classical value to within 5%.

The quasiharmonic approximation includes the correlations in the first quantum corrections, but the algebra of forming the strain derivatives of the normal mode frequencies is lengthy, and the sum over the Brillouin zone must be performed numerically. The results shown in Table I are based on the use of 45 special points to evaluate the Brillouin-zone sum over wave vectors of the triangular lattice.[18] The Hartree theory based on Eq. (B9) gives value for the first quantum corrections to the

TABLE I. First quantum corrections for Lennard-Jones (12,6) model on triangular lattice calculations with three shells of neighbors; functions scaled with σ,ε of Eq. (2.17). Quasiharmonic, Jastrow, and Hartree approximations are as described in Sec. II D.

	$E^{(1)*}/\hbar\omega_E^{*a}$	$\phi^{(1)*}$	$B^{(1)*}$	$C_{33}^{(1)*}$
QHT				
$l^b=1.01$	0.9463	8.26	33.8	21.7
0.985	0.9445	10.20	43.8	26.9
Jastrow				
$l=1.01$	0.9541	8.31	34.1	25.1
0.985	0.9517	10.26	44.1	30.6
Hartree				
$l=1.01$	1	8.81	36.0	29.6
0.985	1	10.87	46.6	36.3

[a]Einstein model zero-point energy $\hbar\omega_E$ from Eq. (B9).
[b]Nearest-neighbor separation L in units of r_0, Eq. (2.17); $l=L/r_0$.

ground-state energy, spreading pressure, and bulk modulus of the Lennard-Jones (12,6) lattice which are within 7% of the quasiharmonic values for l in the range 0.97–1.05. However, the first quantum correction to the shear modulus, calculated from the shift of the normal-mode frequencies under the rectangular deformation Eq. (2.15), is 30% smaller than the Hartree values for the same l range. There is a greater sensitivity of the shear modulus to correlated motions also for three-dimensional solids.[15]

A semiclassical limit for the Jastrow trial energy, Eq. (2.33), is obtained by Gaussian integrations and a running-wave analysis to treat the correlation terms in the trial function. The algebra is similar in complexity to the quasiharmonic theory, and the same method is used to perform the Brillouin-zone sum over wave vectors. Results of the calculations are shown in Table I: The energy, pressure, and bulk-moduli terms are within 1% of the quasiharmonic values, but the shear moduli deviate by 15%. The asymmetric ($\Delta\neq 0$) terms in Eq. (2.33) contribute 10–15 % in the values shown in Table I. On the basis of these comparisons, we expect Jastrow variational calculations to give a less complete treatment of shear moduli than of bulk moduli.

Quantum corrections from the elastic constants C_{12} and C_{11} are constructed from those for C_{33} and B by using Eqs. (2.14) and (2.7). The quasiharmonic value for the first quantum correction to C_{12} on the triangular lattice differs greatly from that for C_{33}. For values of l near 1, Table I, the linear Λ^* term in C_{12} is a much smaller fraction of the classical term than it is for B, C_{33}, and C_{11}.[19] Thus, the first quantum corrections lead to departures from the Cauchy solid condition,[3,13] Eq. (2.12).

The ratio of the squares of the sound speeds, Eq. (2.10), remains close to 3 when calculated with the first quantum corrections for Λ^* up to 0.2 and l near 1; at $l=0.98$, the pressure is positive but the ratio exceeds 3 by less than 3%. Values reported for the ratio for helium monolayers on graphite[2] are much larger than 3; see Sec. III.

E. Generalized Cauchy relation

For a classical, two-dimensional, triangular lattice with only pair potential interactions, the Lamé constants λ and μ are equal,[3,4] Eq. (2.12). The equality is not maintained when quantum effects are included, as the first quantum corrections presented in Table I show.

It has been suggested[4] that the generalization of the Cauchy relation for a quantum solid in a triangular lattice and only pairwise interactions is

$$\mu-\lambda=2(N/A)\langle E_K\rangle\ , \tag{2.38}$$

where N/A is the number density and $\langle E_K\rangle$ denotes the expectation value of the kinetic energy per particle. However, the model calculations do not support this proposal. The quasiharmonic approximation values for the first quantum corrections of the Lennard-Jones (12,6) model presented in Table I give the full linear $\hbar$ term in a semiclassical expansion; with these values the right-hand side of Eq. (2.38) is less than 25% of the left-hand side. The Jastrow calculations for ^{3}He and ^{4}He, discussed in Sec. III B, also do not satisfy Eq. (2.37). For ^{4}He the calculated difference $\mu-\lambda$ decreases with increasing density and even becomes negative for ρ^* near 0.6, while the kinetic energy term increases with increasing density. For ^{3}He, the calculated difference again decreases with increasing density, but it remains positive for ρ^* in the range 0.5–0.6.

III. ELASTIC CONSTANTS OF MONOLAYER SOLIDS

A. Experimental data for quantum monolayers

Goodstein *et al.*[2,20] constructed the compressibility, or bulk modulus, of monolayer solids of ^{4}He and ^{3}He adsorbed on graphite from thermodynamic data. Their values for the bulk modulus are shown in Fig. 1; scalings for helium use $\varepsilon=10.22$ K and $\sigma=2.556$ Å.

The derivation of the shear elastic modulus from thermodynamic data is more complex and depends on further assumptions about the contributions to the elastic constants. For an isotropic elastic continuum the shear modulus C_{33} can be constructed from the Debye temperature, the compressibility, and the spreading pressure; the results for the data presented by Greif and Goodstein[2] are shown in Fig. 2. Greif and Goodstein noted that the Novaco-McTague energy[1] of orientational alignment of the monolayer with the substrate makes a contribution to the shear modulus which they estimated[2] to be 10% or less of C_{33}. In view of the uncertainties as to what the modulated structures of the helium monolayer are,[21] we do not include this term. The values of C_{33} derived with complete neglect of adsorbate-substrate coupling, Fig. 2, serve as a guide to the shear modulus of the helium monolayer; the correction applied by Greif and Goodstein leads to values of C_{33} which are 10% smaller. As discussed in Sec. III B, the discrepancies between our calculations of C_{33} and the data are of order 25%.

The Debye temperatures, reported[22,23] for the low-temperature monolayer solids of argon and of neon on graphite, depend jointly on the bulk and shear moduli.

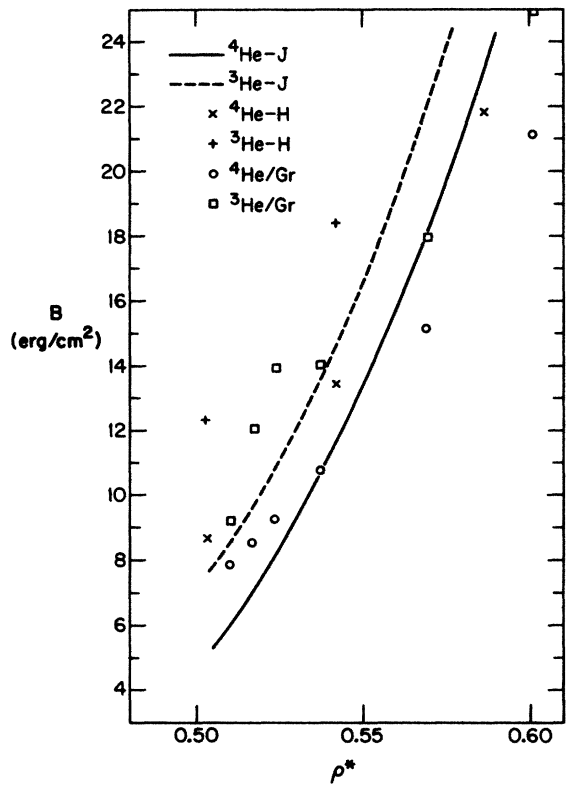

FIG. 1. Bulk modulus of two-dimensional solid helium in erg/cm^2 as a function of scaled density, $\rho^*=\rho\sigma^2$. The experimental data are for ^{4}He (○) and ^{3}He (□) on graphite, from the work of Greif and Goodstein, Ref. 2, and the scaling length is $\sigma=2.556$ Å. The Hartree and Jastrow calculations are described in Sec. II. Related comparisons of chemical potential as a function of area per molecule are shown in Ref. 5. The solid line denotes the Jastrow results for ^{4}He, the dashed line for ^{3}He; the × and + denote the Hartree results for ^{4}He and ^{3}He, respectively.

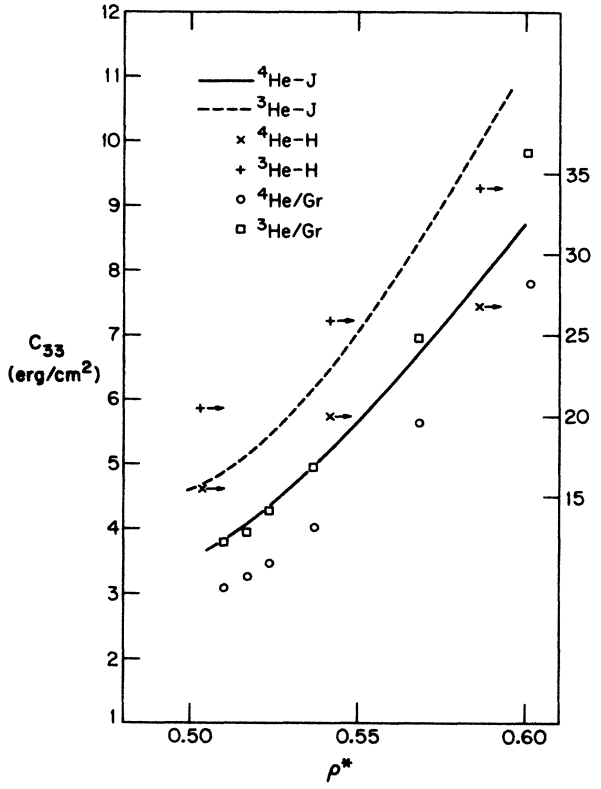

FIG. 2. Shear modulus C_{33} in erg/cm^2 of two-dimensional solid helium as a function of scaled density ρ^*. The experimental values are constructed from the data presented by Greif and Goodstein for ^{4}He and ^{3}He on graphite, Ref. 2, with neglect of effects of adsorbate-substrate coupling, see the discussion in Sec. III A. The Hartree and Jastrow values are for the calculations which include asymmetric terms in the trial functions; see discussion in Sec. II. Labelings are as in Fig. 1; the Hartree results use the right-hand scale.

B. Model calculations

We use the de Boer-Michels values for the Lennard-Jones parameters for helium, $\varepsilon=10.22$ K, and $\sigma=2.556$ Å. These have been used in two previous calculations of helium in mathematical two dimensions.[5,6]

Values for the bulk modulus of the zero-temperature helium monolayer are implicit in a previous report[5] on the chemical potential as a function of coverage for helium adsorbed on graphite, being proportional to the derivative of the (zero temperature) enthalpy with respect to coverage. Values from the Hartree and Jastrow variational calculations for helium are shown in Fig. 1: The results are similar in magnitude to the thermodynamic data.[2] The Hartree values lie above the data; the Jastrow values are below the data at low density and above the data at higher densities. Differences between the calculations and the data are more evident in this presentation than in the previous presentation[5] of chemical potentials.

Results for the helium shear modulus are shown in Fig. 2. The Hartree values are an order of magnitude larger than the values constructed from the data,[2] even including the contribution of the ΔE_2 term, Eq. (2.28), which is 40–50 % of that from the ΔE_1 term for the cases shown in Fig. 2. The values from the generalized Jastrow trial function, Eq. (2.32), are of the order of magnitude of the data and have similar dependence on density, but they are offset from the data by about 25% for the solids of both helium isotopes. The correction terms for noncircular symmetry are included in Fig. 2 and have lowered the values of the shear modulus by 3–7 %.

Values for the ratio R_s, Eq. (2.10), derived from the Hartree and Jastrow approximations for the helium isotopes, are shown in Fig. 3, with values from the data[2] for monolayer helium on graphite. The Hartree approximation to R_s is less than 3 and increases with increasing number density. The Jastrow values range from 2.4 to 4 and also increase with increasing density. By contrast, the ratios for ^{3}He and ^{4}He on graphite constructed from the data of Greif and Goodstein[2] are much larger than 3,

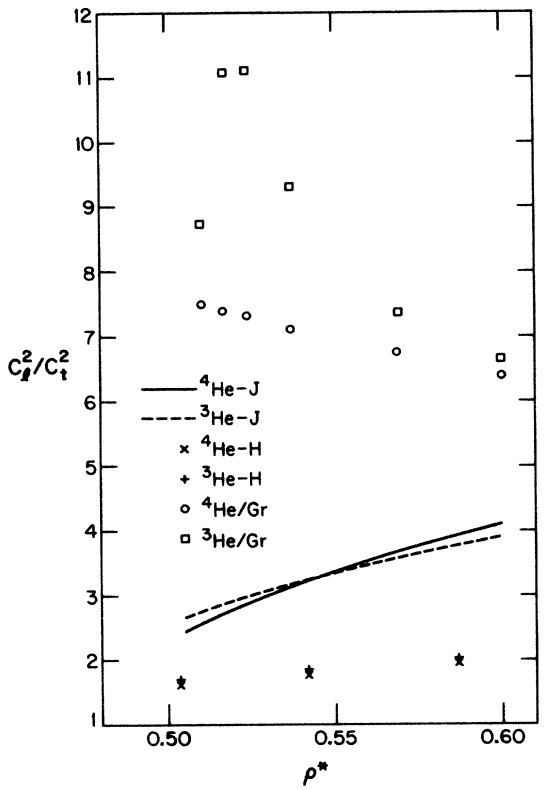

FIG. 3. Ratio of the square of the speeds of sound as a function of scaled density for the two-dimensional helium solids. The ratio R_s, Eq. (2.10), is shown for the helium on graphite (Ref. 2) and for the Hartree and Jastrow approximations to the two-dimensional Lennard-Jones solid. Labelings are as in Fig. 1.

in the range 5–11, and decrease with increasing density. A large part of the calculated increase of R_s with increasing density is due to the increase of the spreading pressure: For ^{4}He the ratio C_{11}/C_{33} increases from 2.0 to 3.2 as the ratio Γ_{11}/Γ_{33} increases from 2.4 to 4.1.

The Debye temperature θ_D is defined in terms of the elastic constants by

$$\theta_D^2 = \left[\frac{2}{\pi}\right]\left[\frac{N}{A}\right]\left[\frac{h}{k_B}\right]^2 \Big/ (1/c_l^2 + 1/c_t^2) , \qquad (3.1)$$

where h and k_B are the Planck and Boltzmann constants and m is the particle mass. This definition gives the characteristic temperature entering in the low-temperature (T^2) specific heat of the monolayer solid; an alternative definition in terms of the zero-point energy of the monolayer has been used by other workers.[9]

Using the QHT quantum corrections of Table I in Eq. (3.1) leads to a value $\theta_D \sim 73$ K for argon at $L = 3.86$ Å (with $\varepsilon = 119.8$ K, $\sigma = 3.405$ Å, and $\Lambda^* = 0.186$). This value is ca. 6% above the value calculated without quantum corrections and is within 10% of the zero-temperature value of 75–80 K extrapolated from Chung's data.[23] The calculated ratio R_s, Eq. (2.10), is 2.9.

The quantum effects are much larger for neon ($\varepsilon = 36.76$ K, $\sigma = 2.786$ Å, and $\Lambda^* = 0.579$).[5] The Hartree calculation gives values for θ_D of 58 K at $l = 1.055$, and 88 K at $l = 1.00$, compared to classical harmonic values 40 K and 72 K, respectively, reported in an earlier work.[24] The Hartree value at $l = 1.055$ is close to a value 55.9 K for the Aziz potential at $L = 3.31$ Å ($l = 1.058$) derived by Moleko *et al.*[9] from self-consistent phonon calculations. There are differences in the models and in the definitions of θ_D in the two calculations, but it appears that the classical harmonic approximation underestimates θ_D by ca. 20% for monolayer neon. The Debye temperatures for monolayer neon on graphite obtained by Huff and Dash[22] are in the range 45–52 K and are below the values from the calculations. The Hartree value for R_s, Eq. (2.10), increases from 2.6 to 2.9 as the solid is compressed from $l = 1.055$ to 1.00, corresponding to the range of monolayer neon lattice constants.

IV. CONCLUDING REMARKS

We have presented a formalism for deriving zero-temperature elastic constants of two-dimensional quantum solids from variational energies. Detailed comparisons among several approximations to the quantum mechanics were made in a near-classical limit, which also applies to such systems as argon and methane. Including site wave-function factors, which are not circularly symmetric for small departures from triangular lattice symmetry, leads to major contributions in the Hartree approximation to the shear modulus. The effect in the Jastrow calculation is smaller, but it should be included in comparisons of calculations to experiment when differences of the order of 10% become significant. An application to the shear modulus of monolayer helium leads to order-of-magnitude agreement between the Jastrow approximation and data for monolayer helium on graphite. The Jastrow approximation again appears to provide a fair account of the role of correlated motions in the properties of the solid.

The calculations used the de Boer-Michels Lennard-Jones (12,6) model for helium because of the advantages of McMillan scaling in forming the Jastrow expectation values. In retrospect, this advantage is not so compelling, because for the finite difference derivatives for the bulk modulus we finally made many Monte Carlo evaluations at a rather fine grid in parameter space. Calculations with a realistic potential model, at a few densities, might not be much more burdensome than our calculations over a range of densities.

The elastic moduli from these calculations may be compared with values derived from the long-wavelength limit of self-consistent phonon calculations, and may be applied to the continuum description of quantum monolayers on a structured substrate.

In a critical analysis of the theoretical side of the comparison of the calculated elastic moduli to the experimental helium data,[2] there are three major unsettled issues: (1) The consequence of using a simple interaction model; (2) the consequence of incomplete functional optimization in the variational quantum mechanics; and (3) what the role of the periodic components of the adatom-substrate potential, neglected here, might be. The first two points may be treated in the future by direct extension and application of methods of quantum solid theory;

we do not believe they lead to major quantitative errors in the results reported here. For the third point, we note that the monolayer helium data extend to a range of large misfits with respect to the graphite substrate. Effects of the substrate periodicity might become smaller at large misfits and this might lead to a closer agreement of the model calculations and the experimental data at higher densities. However, such a trend is not apparent in Figs. 1 and 2 for the bulk and shear moduli, and the discrepancies for the speed-of-sound ratios are large even at the highest densities shown in Fig. 3. The response of a quantum monolayer solid to a periodic substrate field is a subject for much further theoretical and experimental investigation.

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APPENDIX A: LATTICE SYMMETRY TERMS IN THE HARTREE TRIAL FUNCTION

The Hartree trial function, Eq. (2.19), is usually optimized in a class of one-body functions which are spherically symmetric in three dimensions and circularly symmetric in two dimensions. However, Rosenwald[11] included the leading Kubic harmonic K_4 in the trial function in an early Hartree calculation for body-centered-cubic (bcc) ^{3}He, and made a self-consistent solution for the radial functions of the K_0 and K_4 terms. He found a lowering of the variational energy of the order of 10% after inclusion of the K_4 Kubic harmonic. The corresponding effect for the two-dimensional triangular lattice should be much smaller because of the greater isotropy. Our computer programs for the ΔE_2 terms, Eq. (2.28), are easily adapted to provide quantitative estimates of the contribution of a term of sixfold rotational symmetry in the trial function; the treatment is outlined and the results are summarized in this appendix.

The one-body function $\psi(\mathbf{u})$, Eq. (2.27), now has a perturbation of form

$$\tilde{\psi}(\mathbf{u})=\cos 6\theta\psi_6(u) \ . \tag{A1}$$

Expanding the Hartree trial energy for the triangular lattice to second order in γ, the energy lowering is

$$\Delta E_6=\gamma^2\left[2T_2+\frac{\hbar^2}{2m}\int d\mathbf{u}\,|\nabla\tilde{\psi}|^2+\int d\mathbf{u}_1 d\mathbf{u}_2 V_0\,|\psi_0(u_2)\tilde{\psi}(\mathbf{u}_1)|^2-\varepsilon_0\right]+2\gamma T_1 \ , \tag{A2}$$

where ψ_0 and ε_0 are the ground-state solution to Eq. (2.26) and the terms T_1 and T_2 are integrals similar to those defined in Eq. (2.29):

$$\begin{aligned} T_1&=\int d\mathbf{u}_1 d\mathbf{u}_2 V_0\,|\psi_0(u_1|^2\psi_0(u_2)\tilde{\psi}(\mathbf{u}_2) \ , \\ T_2&=\int d\mathbf{u}_1 d\mathbf{u}_2 V_0\psi_0(u_1)\psi_0(u_2)\tilde{\psi}(\mathbf{u}_1)\tilde{\psi}(u_2) \ . \end{aligned} \tag{A3}$$

The functions ψ_0 and ψ_2 of Sec. II B were actually calculated with a circularly averaged potential

$$\bar{V}_0=\int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 V_0(\mathbf{u}_1-\mathbf{u}_2)/(2\pi)^2 \ . \tag{A4}$$

This is not an additional approximation for the angular independent and $\cos(2\theta)$ functions on the triangular lattice, but it is one when used for the $\tilde{\psi}$ of Eq. (A1). For the estimates of this appendix, ψ_6 is taken to be the lowest energy solution of

$$\left[-\frac{\hbar^2}{2m}\nabla^2+\int d\mathbf{u}_2\bar{V}_0\,|\psi_0(u_2)|^2\right]\cos 6\theta_1\psi_6(u_1)=\epsilon_6\cos 6\theta_1\psi_6(u_1) \ , \tag{A5}$$

and the remainder,

$$T_3=\tfrac{1}{2}\int d\mathbf{u}_1 d\mathbf{u}_2 V_0(\mathbf{u}_1-\mathbf{u}_2)\,|\psi_0(u_1)\psi_6(u_2)|^2\cos(12\theta_2) \ , \tag{A6}$$

is included in the evaluation of ΔE_6. However, T_3 for $\Lambda^*=2.67$ and $l=L/r_0$ in the range 1.15–1.48 is less than 0.5% of the difference $\varepsilon_6-\varepsilon_0$, and therefore it is a small correction term.

The result of optimizing γ in Eq. (A2) is

$$\Delta E_6=-T_1^2/[(\varepsilon_6-\varepsilon_0)+2T_2+T_3] \ . \tag{A7}$$

For the Lennard-Jones (12,6) potential, Eq. (2.17), and $\Lambda^*=2.67$ (^{4}He), ΔE_6 is 1% of the Hartree energy calculated with ψ_0 at $l=1.485$, and 0.2% at $l=1.15$; these nearest-neighbor distances, 4.26 Å and 3.30 Å, are near the ends of the range for the monolayer solid on graphite. Values for $\Lambda^*=3.08$ ("^{3}He") are similar. The percentage effect is indeed much smaller than that found for bcc ^{3}He by Rosenwald,[11] and ΔE_6 was omitted from the shear-modulus calculations of this paper.

Similar methods can be used to treat the relative stability of the triangular and square lattices for large de Boer parameter, large lattice dilation, and relatively small spreading pressure. There appears to be no general requirement that the stable lattice be the close-packed triangular lattice under such conditions. The enthalpy as a function of spreading pressure was constructed for the triangular and square lattices for $\Lambda^*=3.08$ (and in less detail for $\Lambda^*=5.0$) for values of l up to 1.9. The Hartree energy for the square lattice was calculated with ψ_0 from Eq. (2.26), using the neighbor shells appropriate to the square lattice, and an energy ΔE_4 corresponding to Eq. (A2) for a perturbation $\cos 4\theta \psi_4(u)$. No regime was found where the square lattice is stable relative to the triangular lattice.

APPENDIX B: FIRST QUANTUM CORRECTION FOR THE HARTREE BULK AND SHEAR MODULI

Application of a first-order quantum correction series for the elastic constants was discussed in Sec. II D. We give the algebraic forms for the Hartree theory in this appendix, first for a general pair potential and then for the Lennard-Jones (12,6) model, Eq. (2.17).

The Hartree ground-state energy per particle of mass m in a triangular lattice of nearest-neighbor spacing L becomes

$$E/N=\tfrac{1}{2}\sum_j \phi(Lx_j)+\hbar\omega_E \ , \tag{B1}$$

$$\omega_E=\left[\sum_j \nabla^2\phi(Lx_j)/(2m)\right]^{1/2} , \tag{B2}$$

with an area per particle

$$A/N=L^2(3/4)^{(1/2)} , \tag{B3}$$

$\hbar$ the reduced Planck constant, and lattice distances in terms of L.

The corresponding approximations for the pressure and bulk modulus follow from

$$\phi=-dE/dA, \quad B=Ad^2E/dA^2 . \tag{B4}$$

The first two terms for the shear modulus

$$C_{33}=\tilde{C}_{33}^{(0)}+\hbar(\tilde{C}_{33}^{(1)}+\Delta\tilde{C}_{33}^{(1)}) \tag{B5}$$

are

$$\tilde{C}_{33}^{(0)}=(1/8L^2\sqrt{3})\sum_j \left[R_j^2\frac{d^2}{dR_j^2}\phi(R_j)-R_j\frac{d}{dR_j}\phi(R_j)\right] , \tag{B6}$$

and

$$\tilde{C}_{33}^{(1)}=\frac{1}{(16L^2m\omega_E\sqrt{3})}\sum_j \left[R_j^2\frac{d^4}{dR_j^4}\phi+3\frac{d^2}{dR_j^2}\phi-(3/R_j)\frac{d\phi}{dR_j}\right] , \tag{B7}$$

and

$$\Delta\tilde{C}_{33}^{(1)}=-\frac{1}{(128L^2m^2\omega_E^3\sqrt{3})}\left[\sum_j \left[R_j\frac{d^3}{dR_j^3}\phi+\frac{d^2}{dR_j^2}\phi-\frac{1}{R_j}\frac{d\phi}{dR_j}\right]\right]^2 . \tag{B8}$$

The corresponding results for the Lennard-Jones (12,6) model are given with lattice sums A_n for a triangular lattice of nearest-neighbor spacing L.[25] The pressure and bulk modulus are obtained from derivatives of the approximate ground-state energy

$$E/N\varepsilon=\tfrac{1}{2}[(A_{12}/l^{12})-2(A_6/l^6)]+\left[\frac{3}{\pi 2^{1/6}}\right]\Omega\Lambda^* , \tag{B9}$$

with

$$\Omega=[2(A_{14}/l^{14})-(A_8/l^8)]^{1/2} , \tag{B10}$$

and

$$l=L/r_0 . \tag{B11}$$

The corresponding terms for C_{33}^* derived from ΔE_1, Eq. (2.25), are

$$C_{33}^*=C_{33}^{(0)*}+\Lambda^*C^{(1)*} , \tag{B12}$$

with

$$C_{33}^{(0)*}=(\sqrt{3}/l^8 2^{1/3})[(7A_{12}/l^6)-4A_6] , \tag{B13}$$

and

$$C_{33}^{(1)*}=[(168A_{14}/l^{16})-(30A_8/l^{10})]/(\pi\Omega\sqrt{6}) . \tag{B14}$$

These are also the terms which would be obtained from an isotropic Einstein oscillator approximation to the solid.

The reduction in C_{33} arising from the noncircular distortion of the (Gaussian) Hartree wave function is a decrease in the $C_{33}^{*(1)}$ coefficient of

$$\Delta C_{33}^{(1)*}=-\sqrt{6}[(7A_{14}/l^{15})-(2A_8/l^9)]^2/(4\pi\Omega^3) ; \tag{B15}$$

the A_2 integral in Eq. (2.29) is second order in Λ^*. For values of l in the range 1.01–1.05, $\Delta C_{33}^{(1)*}$ is $\frac{1}{4}$ to $\frac{1}{3}$ of $C_{33}^{(1)*}$, and thus it is a significant part of the quantum correction.

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